Retention of Stereochemistry at Both Platinum Centres in the Symmetrisation Reaction Between *cis*-[$PtMe_2(PMe_2Ph)_2$] and *cis*-[$Pt(NO_3)_2(PMe_2Ph)_2$]

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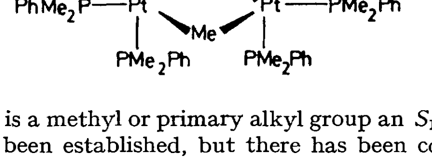
Summary Reaction of *cis*-[$PtMe_2(PMe_2Ph)_2$] with *cis*-[$Pt(NO_3)_2(PMe_2Ph)_2$] in dichloromethane solution gives only *cis*-[$PtMe(NO_3)(PMe_2Ph)_2$] which then isomerises slowly to the more stable *trans*-isomer.

The mechanism of the electrophilic substitution at a saturated carbon atom has been studied in detail, for example in the symmetrisation reaction of R_2Hg (R = alkyl) and HgX_2 (X = halide, nitrate *etc.*) to give RHgX.

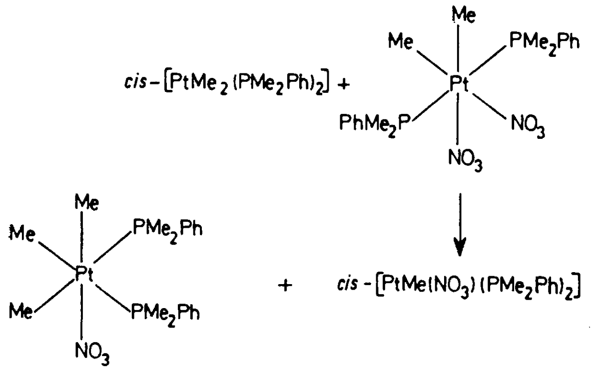


(I)

When R is a methyl or primary alkyl group an S_E2 mechanism has been established, but there has been considerable controversy about whether the transition state is cyclic (with bridging R and bridging X) or open (bridging R only.)[1] Similar reactions of square-planar platinum(II) complexes, which have been studied very little,[2] have the potential advantage that the stereochemistry at platinum during the reaction may be studied.

cis-[$PtMe_2(PMe_2Ph)_2$] and *cis*-[$Pt(NO_3)_2(PMe_2Ph)_2$] react very rapidly in dichloromethane solution to give *cis*-[$PtMe(NO_3)(PMe_2Ph)_2$] as the only product, indicating that the reaction proceeds with retention of configuration at *both* reacting platinum centres. That this is the product of kinetic rather than thermodynamic control is established since the *cis*-[$PtMe(NO_3)(PMe_2Ph)_2$] {n.m.r. in CH_2Cl_2: δ (MeP) 1·53 [d, ^2J(PH) 11 Hz, ^3J(PtH) 52 Hz (*trans* to NO_3)] and 1·43 [d, ^2J(PH) 9 Hz, ^3J(PtH) 15 Hz (*trans* to Me)]; δ (MePt) 0·52 [d of d, ^3J(PH) 7·4 and 7·6 Hz, ^2J(PtH) 47 Hz]} slowly isomerised to the more stable *trans*-isomer {n.m.r. in CH_2Cl_2: δ (MeP) 1·71 [t, $^2J + {}^4J$(PH) 7 Hz, ^3J(PtH) 29 Hz]; δ (MePt) 0·33 [t, ^3J(PH) 7 Hz, ^2J(PtH) 85 Hz]} when set aside in solution.

Substitution reactions at platinum(II) usually take place with retention of configuration by way of a trigonal-bipyramidal intermediate in which the entering and leaving groups and the *trans* ligand are in the equatorial plane,[3] and



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the stereochemical course of the present reaction can be understood if a cyclic intermediate such as (I) is formed with bridging methyl and nitrate groups. The geometry of each platinum atom is trigonal bipyramidal, and the intermediate would be expected to break down to give *cis*-[PtMe(NO_3)(PMe_2Ph)$_2$] only.

Methyl for nitrate exchange reactions also occur rapidly between platinum(II) and platinum(IV) complexes. The stereochemical course of the reactions are more difficult to study, but preliminary results suggest that the reaction in the Scheme takes place as shown, with retention of configuration at platinum(II) but loss of configuration at platinum(IV).† It is possible that ligand dissociation from platinum(IV), thus creating a vacant co-ordination site, is necessary before the exchange reaction can take place, in which case the change of configuration at platinum(IV) during the reaction is not surprising.

(*Received*, 1*st September* 1975; *Com.* 990.)

† A simple exchange reaction is indicated rather than the alternative redox mechanism involving transfer of Me and NO_3 groups from Pt^{IV} to Pt^{II} by deuterium labelling experiments, but the reaction is complicated because the [Pt(NO_3)Me_3(PMe_2Ph)$_2$] formed undergoes subsequent reductive elimination of ethane giving *trans*-[Pt(NO_3)(Me)(PMe_2Ph)$_2$].

[1] O. A. Reutov and I. P. Beletskaya, 'Reaction Mechanisms of Organometallic Compounds', North-Holland, Amsterdam, 1968, ch. 2; M. H. Abraham in 'Comprehensive Chemical Kinetics', Vol. 12, eds., C. H. Bamford and C. F. H. Tipper, Elsevier, Amsterdam, 1973, ch. 3 and 5.
[2] R. J. Puddephatt and P. J. Thompson, *J.C.S. Dalton*, in the press.
[3] C. H. Langford and H. B. Gray, 'Ligand Substitution Processes', Benjamin, New York, 1965, ch. 2.